# Optical Thin Films by Wet Chemical Processing

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## Abstract

Wet chemical processing of ceramics, glasses and inorganic-organic hybrids in the form of films has a large number of both proven and potential optical applications. The present review will focus on progress since 1990 in the areas of ferroelectric films, electrochromic and photochromic films, planar waveguides, and NLO films. Where appropriate, advances will be illustrated by results obtained in our laboratories.

## Introduction

The field of optical thin films has benefitted from multidisciplinary research efforts which have led to numerous recent advances, the most notable being improved film performance (near-bulk properties) and new multifunctionality (e.g. incorporation of organic dyes in organic-inorganic composite materials). The present paper will focus on a range of important types of optical thin films which have been prepared using wet chemical techniques, with emphasis on results reported since 1990 and where appropriate with results obtained in our laboratories. For reasons of space, discussion of interesting topics such as transparent conductors, inorganic planar waveguides, surface patterning and solid state dye lasers had to be deferred.

## A. Ferroelectric (FE) Films

FE films are increasingly important for a myriad of applications in both optics and electronics. FE films are versatile and multifunctional, and exhibit a variety of technologically-useful properties. The optical properties of sol-gel derived FE films have recently been reviewed by the authors [1]; and only two characteristics of these films, which impact optical and electrooptic (EO) devices, will be discussed here - viz. optical attenuation and linear EO coefficients.

Table 1 shows the optical losses of various FE films. Such films exhibit low attenuations (2 dB/cm) when fired at low temperatures to obtain grain sizes. The lowest waveguide attenuation for any crystalline PLZT film was obtained for a sol-gel PLT 28 film. Such waveguides exhibit a loss of only 1.4 dB/cm, which is much lower than that of even single crystal films on epitaxial substrates prepared by other methods. This low attenuation attests to the high degrees of chemical homogeneity and stoichiometry of the films despite their complex multicomponent nature. We have also found PZT 53/47 films can be densified without crystallization. The losses of the resulting amorphous films, with refractive indices $\underline{n} > 2$, were only 1.1 dB/cm.

Table 2 shows the linear EO coefficients of various FE films and bulk FE's. The highest values are obtained for films deposited epitaxially on selected substrates. Work performed in our laboratory has indicated that reasonably high values can be obtained for polycrystalline PLT 28 films without the need for expensive single crystal substrates. This value is even better than sputtered $LiNbO_3$ films or even bulk $LiNbO_3$.

Table 1. Optical Losses of selected FE films.

| FE Film | Loss ( dB/cm) at 6328A | Reference |
|---|---|---|
| PLT 15 | 8.0 | This work |
| PLT 28 | 1.4 | This work |
| Sputtered epitaxial PLT 28 | 6.0 | 2 |
| Sputtered single crystal PLT 28 | 5.0 | 3 |
| Sol-gel $BaTiO_3$ | 1.2 - 2.6 | 4 |
| Sol-gel $LiNbO_3$ | 2.2 | 5 |
| Sputtered $LiNbO_3$ | 0.9 | 5 |

Table 2. Linear EO Coefficients of FE films

| FE Film | Linear EO Coefficient (pm/V) | Reference |
|---|---|---|
| Sol-gel PZT 65/35, epitaxial | 108 | 6 |
| Sputtered PLT 24, epitaxial | 81 | 7 |
| Sol-gel PLT 28 | 56 | This work |
| Sol-gel PLZT 8/65/35 | 30 | 8 |
| Sputtered PLT 21 | 28 | 7 |
| Sol-gel PZT 60/40 | 24 | 9 |
| Sol-gel $LiNbO_3$ | 7.2 | 5 |
| Sputtered $LiNbO_3$ | 1.34 | 10 |
| Bulk PLZT 8/40/60 | 102 | 11 |
| Bulk $LiNbO_3$ | 16 | 11 |

## B. Magnetooptic Films

Garnet films, e.g. yttrium iron garnet (YIG) and yttrium aluminum garnet (YAG), are used extensively in microwave applications, as well as in the area of magnetooptics (MO). The latter uses include MO data storage, thin film waveguide isolators, phase shifters, rotators and light modulators. Garnet films are preferred over metallic MO materials such as GdTbFe and Co-Pt alloys due to their environmental stability and low optical absorption in the visible. The Faraday rotation, $\theta_F$ - the rotation angle of polarized light transmitted per unit length of material - is an important parameter in many MO applications.

Wet chemical techniques have been used to prepare YIG and doped YIG films [12-15]. The garnet structure, as typified by YIG, readily accommodates a large number of dopants including rare earths or Bi in the dodecahedral Y sites, and La, Al or other Group III elements in the octahedral and tetrahedral Fe sites. The wide latitude in doping , made easier in wet chemically derived films, leads to a large window of opportunity in tailoring the properties of the materials over a considerable range. Attention in the area of YIG research has focussed on incorporating high Bi contents into the garnet films, e.g. $Y_{3-x}Bi_xFe_5O_{12}$. Addition of Bi not only enhances $\theta_F$ but also lowers the temperatures where the garnet phase first nucleates

and single-phase crystalline garnet films are achieved. Work performed in our laboratories also indicated that Bi tended to enhance the overall crystallinity of the garnet films.

Values of x up to 2.5 and 2.3 have been reported in sol-gel derived and LPE films, respectively [12]. While the compositional range of Bi-YIG films is higher in sol-gel derived films than in LPE films, sol-gel BIG films have yet to be reported (in contrast to reports of sputtered BIG films [14]). For a given composition (especially with Bi content, x > 1.5), sol-gel synthetic routes appear to produce films with higher $\theta_F$'s than other techniques. At high Bi content (x > 2.5), non-garnet extraneous phases such as $Bi_2Fe_4O_9$ [12], $Bi_2O_3$, a-$Fe_2O_3$, $BiFeO_3$ or $YFeO_3$ [13] appear in wet chemically derived garnet films after firing. This suggests chemical inhomogeneity in the films. Bi ions are quite volatile and labile; and the precise control of Bi content is probably the most important processing factor in achieving high quality garnet films.

## C. Electrochromic Films

Numerous metal oxide thin films have been studied for their electrochromic (EC) activity. Most of these have been deposited by vacuum deposition techniques, but sol-gel technology offers the advantage of depositing EC coatings using low cost capital equipment. New deposition techniques will be required to deal with large areas, single sided coating and curved surfaces. Also required are EC films with well-defined stoichiometry and microstructure [16-18].

EC films prepared by the sol-gel method are listed in Table 3. These are divided into films which are cathodic or anodic for coloration and those which are colored or colorless in both states.

Table 3. Sol-Gel Derived Electrochromic Films

| Cathodic for Coloration | Anodic for Coloration | Colored or Colorless in both States |
|---|---|---|
| $WO_3$ [19-24] | $IrO_2$ [21] | $V_2O_5$ [22,26,28] |
| $TiO_2$-$WO_3$ [20,21,25] | NiO [21,27] | $Na_{0.33}V_2O_5$ [29] |
| $MoO_3$-$WO_3$ [20,21,31] | | $NbVO_5$ [30] |
| $TiO_2$ [28,35] | | $TaVO_5$ [30] |
| $MoO_3$ [20,21] | | $TiO_2$-$CeO_2$ [34,35] |
| $Nb_2O_3$ [32,33] | | |

Of the EC materials listed in Table 3, $WO_3$ has been the most widely studied. Its advantages are its high coloring efficiency, low cost and ease of deposition by a variety of techniques. Sol-gel $WO_3$ has been prepared using many different precursors, including alkoxides, chlorides, colloidal solutions, peroxytungstic acid peroxotungstic ester [20,36]. The last method has the advantage of low-cost starting materials, stable precursor solutions, and the ability of controlling the microstructure and thickness of the $WO_3$ film by simply adding oxalic acid to the dipping solution [37]. Using this method, carbon-free fired coatings with thickness greater than 0.5$\mu$m are obtained by a single dip. Addition of 32% oxalic acid to the dipping solution result in coatings which, when heated to 250C, have a crystalline/amorphous hybrid structure. In contrast, using a dipping solution without oxalic acid gives a substantially amorphous structure [38]. Oxalic

acid in the dipping solution was also found to enhance the optical and electrochemical cycling properties of the fired films.

Admixtures of metal oxides to $WO_3$ have been used to improve its electrochromic behavior and cycling properties. Several groups have prepared sol-gel thin films of $WO_3$ doped with $TiO_2$ [39-41]. Additions of $TiO_2$ precursors to the tungstic sol-gel solutions increased solution stability, improved coating quality and increased the cyclic lifetime of amorphous $WO_3$. This was related to a reduction in the number of defects where $Li^+$ ions can bind irreversibly to the matrix [42]. The enhanced cyclability was, however, achieved at a loss of coloring efficiency compared to undoped $WO_3$ coatings.

The coloring efficiency of $WO_3$ films increases considerably when doped with about 0.8 atomic percent Mo [43]. The change occurs primarily because the peak of the absorption spectrum after doping shifts from 1.3 eV to about 1.7 eV, resulting in a deeper color in the visible part of the spectrum. The maximum shift in the absorption spectrum occurs for a molar ratio W:Mo of 7.3 [44]. Mo- doped $WO_3$ coatings have also been prepared using precursors based on halides [20] and peroxo complexes [21].

An EC device is composed of many layers, one of which is the EC active layer. Other layers include an ion storage layer or "counter electrode" and an electrolyte. All of these layers can be produced by sol-gel methods, as shown by Judeinstein [45] and Chemseddine [46]. Choices for the counter electrode include $TiO_2$-$CeO_2$ [31] and $V_2O_5$ [28]. Proton-conducting electrolytes have been prepared from a $TiO_2$ gel organically modified by glycerol [45]; but the long-term cyclability of these devices is unknown and the stability of the gel electrolyte has not been established.

Mo and Nb oxides have been suggested as alternative EC electrodes to $WO_3$. All three of these films color by the double insertion of an electron and a proton or alkali ion. $MoO_3$ in the reduced state has a dark blue color; but its ability to color is poorer than that of $WO_3$ [48]. It has been synthesized by the sol-gel method using halogenated [20] and peroxo [21] compounds. Recently, Avellaneda et al [33] have prepared EC thin films of $Nb_2O_5$. The best results were for crystalline films heated to 560C in oxygen for 3 hrs. The coating showed almost 100% reversibility to $Li^+$ insertion, high chemical stability, and an optical modulation in transmission both in the visible and near infrared from 80 to 20% for a coating 200 nm thick. The coating in the reduced state was deep blue.

## D. Photochromic Films

Much attention has been given to the phenomenon of photochromism (PC) because of its wide range of applications [49]. Photochromic materials change their light absorbing properties when optically excited and the induced coloration can remain even after the excitation source has been removed. PC coloration involves the trapping of electrons at appropriate sites within the material, which promotes light absorption.

The most studied thin film PC materials have been $WO_3$, $MoO_3$ and $V_2O_5$, deposited by vacuum techniques [50,51]. The density, degree of crystallinity [52] and water content [51] of evaporated $WO_3$ films play a critical role in PC behavior. All of these coatings have been prepared by sol-gel methods; but there are few studies of their PC behavior. Lee et al [53] studied the PC behavior of alkoxide-derived thin films of $WO_3$. Similar to evaporated films, the PC behavior depended on the microstructure of the coating.

Mennig et al [54] investigated PC in sol-gel thin films of sodium aluminoborosilicate containing nanosized crystallites of AgCl. The coatings were synthesized from TEOS, methyltriethoxysilane, trimethylborate and aluminum isopropoxide. The dried coatings were impregnated with $AgNO_3$ from an ethanol solution. AgCl was formed by exposure of the film to HCl vapor. On exposure to UV light, the coatings turned brown-violet. To bleach the coatings back to high transparency, a thermal treatment of about 400C was needed. The PC behavior of these coatings is attributed to the reversible formation of Ag colloids about 5 nm in size from AgCl particles about 40 nm in size, and provides an unexplainably-intense

modulation of light. Thin films showing PC activity have also been made by incorporating PC dyes into a sol-gel silica matrix [55].

## E. Passive Waveguides

Passive optical waveguides are fundamental to the technology of integrated optics [56]. Because the waveguide is responsible for guiding light to various components, it is essential that the waveguide exhibit low loss. Unlike optical fiber communication applications, where transit distances are measured in km, integrated optical applications require good signal strength over distances of only a few cm. As a result, planar waveguides with losses < 1 dB/cm, preferably $\leq$ 0.1 dB/cm, are usually of sufficient quality for applications. Primary sources of loss include absorption, Rayleigh scattering from index inhomogeneities in the volume of the film and from interface/surface roughness [56,57,58], and Mie scattering from larger film defects and inclusions.

Sol-gel synthesis of planar waveguides has received much attention in the past decade because of the ease with which films can be made by spin and dip coating. Also, the $\underline{n}$ of the film is easily tailored by altering the chemical composition of the solution [59], and homogeneous mixing can be obtained at the atomic level [58], which reduces volume scattering. The sol-gel process also offers a promising alternative to conventional techniques for the fabrication of waveguides incorporating surface-relief structures. Many sol-gel planar dielectric waveguides are silicate-based e.g., PbO-SiO$_2$ [60] and SiO$_2$-TiO$_2$ [58,59,61-63]; but recent years have seen the emergence of promising organic-inorganic hybrid waveguides as well. These will be focus of the present discussion.

Organically modified ceramics, variously known as Ormosils, Ormocers or Polycerams, are hybrid materials in which the organic and inorganic functionalities are combined during synthesis. Schmidt et al. reported that Polyceram waveguides with low optical loss can be synthesized [64-66]. Methacrylate-substituted silanes were copolymerized with methacrylic acid (MA), which in turn were used as a chemical links to the inorganic component (ZrO$_2$) to obtain slab waveguides with losses of 3 to 6 dB/cm at 633 nm [64]. The losses were attributed to scattering from dust particles in or on the coating. The processing was optimized to obtain thick layers (up to 20 $\mu$m in thickness) with losses of 0.1 dB/cm or less [65]. This low loss can be explained in terms of mode confinement: the thicker the waveguiding layer, the lower will be the loss provided that volume scattering is minimal.

Sorek et al [67] synthesized planar waveguides of TiO$_2$-$\gamma$ glycidyloxipropyltrimethoxysilane (GLYMO). The refractive index, $\underline{n}$, increased and film thickness decreased with increasing TiO$_2$ content. Losses of 2 dB/cm were found for the TE$_0$ mode, and 3 dB/cm for higher (TE$_1$-TE$_2$) modes, indicating that the scattering was due mainly to imperfections at the interfaces.

Since a portion of the optical loss in a slab or channel waveguide is due to scattering at the air and substrate interfaces, it is useful to embed the waveguiding layer in layers with lower $\underline{n}$ - i.e. to include a buffer layer on top of the substrate, and a cladding layer on top of the waveguide. Recent experiments have shown a loss of < 0.5 dB/cm in such slab structures [66].

Work in our laboratory has shown that the incorporation of Ti and Si alkoxides in (N-triethoxysilyl propyl) O-polyethylene oxide urethane (MPEOU) [68,69] and polydimethylsiloxane (PDMS) results in easy formation of crack-free planar waveguides. By varying the organic/inorganic content, refractive indices as high as 1.685 and attenuations as low as 0.15 dB/cm can be obtained - *even for thin waveguides without buffer or cladding layers*. The waveguides exhibit superior thermal and mechanical properties compared with the constituent polymers. The incorporation of chelating agents such as 2,4 pentanedione decreases the surface roughness of the waveguides and the resulting attenuation [69,70]. AFM shows that the appropriate chelate can result in a RMS surface roughness as small as 1.22 Å. Also investigated have been thin planar

waveguides fabricated from Polycerams containing other inorganics, such as Zn, Zr, Pb, Ge and Ta. The typical losses of such waveguides are in the range 0.15 -3 dB/cm.

In order to understand the source of loss in the Polyceram waveguides, the MPEOU-SiO$_2$-TiO$_2$ and PDMS-SiO$_2$-TiO$_2$ systems with different polymers but similar inorganic content were studied. The loss decreased with increasing mode number for MPEOU-SiO$_2$-TiO$_2$ waveguides, but increased with mode number for PDMS-SiO$_2$-TiO$_2$ waveguides. These results combined with electric field profiles indicate that the loss is mainly due to volume attenuation in the MPEOU-SiO$_2$-TiO$_2$ system, and mainly due to surface scattering in the PDMS-SiO$_2$-TiO$_2$ system.

Mie scattering calculations were conducted for the MPEOU-SiO$_2$-TiO$_2$ system and the results were compared with measured attenuations. The loss data were inconsistent with heterogeneities larger than about 15Å in radius. Further, the calculations show that the loss is proportional to the square of the density difference between particle and host. Hence, as the refractive index of the inorganic component increases, the loss should increase strongly. Upon varying the TiO$_2$/SiO$_2$ ratio over the range 0/1 to 2/1, with corresponding changes in $n$ of the inorganic component from 1.46 to 1.77, the measured loss showed no correlation with TiO$_2$/SiO$_2$ ratio. Still further, high resolution TEM studies of PDMS-SiO$_2$-TiO$_2$ Polycerams of the same polymer content with TiO$_2$/SiO$_2$ = 2/1 indicate the absence of any observable inhomogeneities. Hence it is concluded the inorganic and organic components of these Polycerams do not occur as separate phases. Rather they are apparently interspersed on a scale approaching the molecular; and the resulting materials can be viewed as molecular composites.

Although inorganic waveguides can also be fabricated with low optical attenuations, they typically cannot be obtained in thicknesses greater than about 0.5 $\mu$m. The ease of processing Polycerams, including low temperature processing, together with the ability to fabricate them as waveguides of arbitrary thickness, make these materials highly attractive for integrated optics applications. In addition, recent loss studies on MPEOU-SiO$_2$-TiO$_2$ waveguides have revealed that the loss remains constant up until temperatures as high as 125C, thus rendering Polycerams suitable for higher temperature applications.

## F. Quantum Dots

Semiconductor-doped glasses have attracted interest for applications in photonics due to the quantum-size effect which leads to high $\chi^3$ nonlinearity. The semiconducting crystallites, such as CdS and CdTe, are randomly oriented within a glass matrix and homogeneously distributed as small clusters. These quantum dots or Q-particles usually contain 10-500 atoms and are 1-10 nm in diameter [71].

Sol-gel processing offers a useful route for controlling the particle size and distribution of Q-clusters. Fairly narrow size distributions have been achieved with standard deviations of 0.4 nm [72]. Also, high concentrations of semiconducting crystals up to 20 wt% of CdS in SiO$_2$/PDMS have been achieved [73]. In addition, sol-gel processing is attractive for incorporating a wide variety of semiconducting crystals. Both solution derived and diffusion derived sol-gel routes have been used. In the first method, semiconductors or metals in the form of various precursors are mixed with metal alkoxides and a gel is formed. The homogeneous distribution of precursors favors uniform growth of the crystals during firing. Nogami et al[74], e.g., prepared CdTe quantum dots from TEOS and CdTeO$_4$:2H$_2$O precursors. After firing in H$_2$ gas, cubic CdTe crystals with sizes of 2.5 to 4.3 nm were obtained, depending on the processing conditions. A linear relation was found between the absorption edge energy and the inverse square of the particle diameter. Nogami et. al. have also prepared Q-dot sol-gel glasses with CdS [75], PbS [76], CdSe [77], CuCl [78], and CuBr[79] particles. CdS and ZnS doped silica glasses have also been prepared from thiourea complexes. An increase in the particle size and distribution was observed at higher complex concentrations [80].

The second method takes advantage of the uniform pore diameters of gels. Selected precursors can be diffused within the pores of a gel and reacted to provide controlled precipitation of the semiconducting clusters. Sol-gel glasses have been synthesized with pore size distributions within 5% [81]. These were used to form ZnS clusters in aluminoborosilicate gels by soaking the glass in $(CH_3CO_2)_2Zn$ followed by reaction with $H_2S$ at 100C. As the pore size decreased, the cluster size also decreased, as evidenced by a blue shift in the absorption edge. The crystal size was shown to depend on the concentration of the metal oxide within the gel as well as reaction time and temperature [71]. Others have used similar methods to form various clusters in amorphous and crystalline hosts [82-84]. Nonlinear properties were measured by third harmonic generation (THG) and found to be orders of magnitude higher in sol-gel systems when compared to polymer hosts [85]. $\chi^3$ values of sol-gel glasses containing Q-particles are typically about $10^{-7}$ -$10^{-6}$ esu under resonant condition [86] and $10^{-12}$ - $10^{-11}$ esu under nonresonant conditions [73,87]. By comparison, commercially available semiconductor doped glasses used as sharp cut filters have $\chi^3$ values of $10^{-11}$-$10^{-7}$ esu [85].

Still further work is required to increase the concentration of Q-particles while maintaining a small particle size and narrow distribution. Also, a balance must be made between an increase in concentration and the need to minimize absorption and scattering losses. These can only be achieved by careful control of pore size and distribution, diffusion of semiconducting precursors, thermal treatment, and annealing processes.

## G. Nonlinear Optic (NLO) Organics

Nonlinear optical processes, in which the optical properties of materials are intensity dependent, are attractive for many technologies. NLO organic dyes and inorganic crystals are the chief candidate materials. NLO organic dyes have advantages for use in integrated optics including ease of fabrication, lower dielectric constants, higher bandwidths, low temperature processing, faster response times, and higher electro-optic (EO) and NLO responses with increased concentration [88,89]. Unfortunately, NLO organics lack the optical, thermal, and mechanical properties to be used alone, and must be incorporated within a host (e.g., polymers, glasses, Polycerams).

Orientation of the dye is required for NLO response, and large values of $\chi^2$ are required (as 60 pm/V) for practical applications [90]. High concentrations and alignment of the NLO chromophores are needed, as are orientational, thermal, and chemical stability, and optical transparency. Chromophore alignment has been achieved by applying large electric fields via contact poling or by corona discharge methods.

A variety of NLO dyes have been incorporated in sol-gel glasses and Polyceram films [91-99], and the area has been summarized in several reviews [100-102]. The sol-gel route offers a rigid matrix, high Tg, tailorability of optical properties through compositional variations, and high laser damage thresholds. For example, Polyceram hosts can withstand high power densities ($>500$ MW/cm$^2$) compared with polymers (60 MW/cm$^2$) [103]. SHG has been reported even for unpoled Polyceram films [97], likely reflecting orientation of the dye at inorganic-organic interfaces in the films. In all cases, poling increases the SHG intensity; but poling at elevated temperatures can result in significant sublimation of the dye [92,94,98]. In 4-(dimethylamino)-4'-nitrostilbene (DANS)/TiO$_2$ composites, higher dye loadings did not show an equivalent increase in the SH intensity [99], suggesting that aggregation and/or crystallization may occur.

To circumvent some of these problems, numerous silylated NLO dyes, as N-[3-(triethoxysilyl)propyl]-2,4-dinitropheylamine (TDP) [104-108], silylated pNA [109,110], and silylated azobenzenes [111-113], have been incorporated within sol-gel matrices. Improved temporal stability of dye orientation in these materials compared with conventional dye-doped sol-gel glasses, has been reported [99,112,114]. Dye extraction studies, performed in our laboratory, have shown that processing conditions greatly affect how

much of the silylated dye is bonded within the matrix, and that with proper processing extraction of dye the can be eliminated [115]. The use of functionalized dyes allows for the addition of high concentrations of chromophores without aggregation and the potential for improved macroscopic NLO properties.

High rigidity or crosslinking of the sol-gel matrix results in the immobilization of the NLO dye. This is required to obtain high temporal stability. The matrix rigidity is a function of sol-gel processing parameters (e.g. $H_2O$ content) [108,116]. Optimally, the dye/matrix crosslinking should take place during poling to achieve highly oriented, relaxation-free NLO nanocomposites.

In addition to sol-gel processing conditions, details of the poling procedure can have a significant effect on the degree of orientation and the temporal stability. Corona poling of thin films is preferred because a top electrode is not required, poling can be achieved over large areas, and macroscopic shorts do not occur due to defects in the film [90]. The corona poling dynamics of NLO chromophores, monitored by SHG while poling [117,118], confirm two processes, molecular orientation and charge deposition or decay[119]. Orientation has been successful at room temperature, but elevated temperatures provide a larger degree of orientation; and temporal stability improves with heat treatment and longer poling times, presumably due to increased crosslinking locking the dye in place [99,108,120]. Also, higher corona poling currents increase the degree of orientation of dye found with TDP/$SiO_2$-$TiO_2$/triethoxysilyl modified poly(ethylene oxide) Polycerams [121].

For $\chi^3$ materials, the issues are different. All materials have inherent third order nonlinearities and orientation is not required to observe the nonlinearity. The nonlinear refractive index required for all-optical switching devices is about $\chi^3 = 10^{-11}$ to $10^{-10}$ esu. Also, a waveguide device criterion ($\alpha*L < 1$), where $\alpha$ is the loss and L is the length of the device, needs to be maintained. For a waveguide device which is 1 cm long, losses must be below 1 cm$^{-1}$ [122,123]. Conjugated polymers, which have extensive $\pi$-electron delocalization, have high nonresonant third-order nonlinearities ($> 10^{-10}$ esu), but lack good optical properties (e.g., poor attenuation) [101]. To circumvent such problems, these conjugated polymers have been incorporated within sol-gel matrices to improve the optical and mechanical properties, as well as the environmental stability. Numerous polymers such as poly(thienylene vinylene) (PTV) [124], polyaniline [125], and Poly(p-phenylene vinylene) (PPV) [126] have been incorporated within sol-gel silica hosts. $\chi^3$ values in the $10^{-10}$-$10^{-9}$ esu range have been measured by degenerate four wave mixing (DFWM) with PPV/$SiO_2$ composites [127]. The number of conjugated polymers which can be incorporated within sol-gel hosts is limited due to solubility problems. To achieve higher $\chi^3$ values, higher concentrations of polymer are needed, but insolubility and phase separation between the organic and inorganic components makes this difficult. Regardless, composites containing 50 weight % polymer have been fabricated [126].

## Conclusions

Notable progress has taken place during the past 4 years in the area of sol-gel derived optical films. In areas ranging from ferroelectric films and electrochromic and photochromic layers to Polyceram waveguides, research advances have led to ongoing commercial explorations. This last development seems particularly significant, and augers well for the future. It also reinforces our previous plea of four years ago for greater interaction among chemists/materials technologists and device engineers. We in the materials community can synthesize a very broad range of optical coatings, often with novel microstructures, phase assemblages and properties. The full potential of these advances requires, however, input from the device community as to critical needs and important opportunities. The coming years will hopefully see such collaboration, with more sol-gel inventions converted to innovations.

## Acknowledgments

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